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UCRL-JRNL-228049

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February 14, 2007

Journal of Solution Chemistry

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Abstract

The four diffusion coefficients D_{ij} of the ternary system NaCl-$MgCl_2$-H_2O at the simplified seawater composition 0.48877 mol·dm^{-3} NaCl and 0.05110 mol·dm^{-3} $MgCl_2$ have been remeasured at 25 °C. The diffusion coefficients were obtained using both Gouy and Rayleigh interferometry with the highly precise Gosting diffusiometer. The results, which should be identical in principle, are essentially the same within or very close to their combined "realistic" errors. This system has a cross-term D_{12} that is larger than the D_{22} main-term, where subscript 1 denotes NaCl and 2 denotes $MgCl_2$. The results are compared with earlier, less-precise measurements. Recommended values for this system are $(D_{11})_V = 1.432 \times 10^{-9}$ m^2·sec^{-1}, $(D_{12})_V = 0.750 \times 10^{-9}$ m^2·sec^{-1}, $(D_{21})_V = 0.0185 \times 10^{-9}$ m^2·sec^{-1}, and $(D_{22})_V = 0.728 \times 10^{-9}$ m^2·sec^{-1}.

Keywords Diffusion · NaCl-$MgCl_2$-H_2O · Seawater · Ternary system · Multicomponent systems

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1. Introduction

Diffusion coefficients are of considerable interest in modeling geochemical processes in seawater. The system NaCl-$MgCl_2$-H_2O is the most realistic second-order model of this system, the first-order one being NaCl-H_2O and the third-order one involving the constituents Na-Cl-Mg-SO_4.

This paper is one of a series reporting the diffusion coefficients of the system NaCl-$MgCl_2$-H_2O at 25 °C. The first five papers [1–5] reported a systematic study of this system from a total concentration of 0.25 mol·dm^{-3} to near saturation at 5 different solute

mole ratios, using the highly-precise Gosting diffusiometer [6]. That study was part of an international collaboration, begun in 1984, to determine the thermodynamic and transport properties of an aqueous mixed-valence, ternary, strong-electrolyte solution. The purpose was to provide data for the whole range of compositions for future testing of electrolyte theories and of semi empirical estimation methods based on Irreversible Thermodynamics. The NaCl-$MgCl_2$-H_2O system was chosen in part because the corresponding thermodynamic work had already been completed and in part because, as noted above, these solutes are the major constituents of seawater and its evaporites. Paper 6 [7] contains data at 35 °C for three solute mole ratios near saturation.

The seawater composition studied here, NaCl (0.48877 mol·dm^{-3})-$MgCl_2$ (0.05110 mol·dm^{-3})-H_2O, is an extension of that systematic set of compositions. The experimental work was done in 1988, shortly after the work reported in paper 5 [5], and was also aimed at comparing the results of the Rayleigh and Gouy interferometric methods of diffusiometry. Publication has been delayed for reasons beyond our control.

Some of us had previously investigated the seawater composition [8,9] using a less precise Rayleigh diffusiometer, an adapted Beckman-Spinco Model H electrophoresis apparatus. These older results agree fairly well with our new, more accurate results, and will be compared below.

Our first investigation of the seawater system in 1973 [8] was also the first attempt by anyone to obtain diffusion coefficients for a ternary system using Rayleigh interferometry. Because of subsequent improvements in the optics, alignment, and data analysis, we hesitated to publish these first results. Our second investigation, published in 1986 [9], used the more optimized Model H configuration [10]. However, subsequently we had concerns for both investigations about the analyses for Mg in the $MgCl_2$ in the 1973 work, the various preparations of the solutions, and the effect of the double pass of light through the Model H optical system. Consequently, when the highly-precise single-pass Gosting diffusiometer [6] became available to us at LLNL and we had several more years of experience, it seemed desirable to redo this important geochemical system.

We note that optical interferometry methods are the most accurate for liquid-solution diffusion measurements, and of these Rayleigh and Gouy have been the most highly developed. They should, of course, give the same results for perfect experiments and lenses. The apparatus used, the Gosting diffusiometer, then at Livermore, has both optical systems and could be switched between them in less than 2 minutes. Therefore, we could measure both types of fringe patterns alternatively using exactly the same cell and same solutions. We will find that ternary diffusion coefficients D_{ij} from the two optical arrangements are the same within "realistic" experimental errors.

Because the concentration differences are small in these free-diffusion measurements, our results are referred to the *volume-fixed* reference frame, denoted using a subscript V. If 1 and 2 refer to the solutes NaCl and $MgCl_2$, respectively, then the flows $(J_i)_V$ are related to the concentration gradients in one dimension $\partial C_i/\partial x$ in mol·dm^{-4} by

$$(J_i)_V = \sum_{j=1}^{2} (D_{ij})_V \left(\frac{\partial C_j}{\partial x}\right) \qquad i = 1, 2 \qquad (1)$$

where C_i are the concentrations in mol·dm^{-3}, x is the vertical distance in 1 dimension in dm and the $(D_{ij})_V$ are the volume-fixed diffusion coefficients in m^2·sec^{-1}.

We will find a large D_{12} cross term, approximately the same size as D_{22}.

2 Experimental

The experimental techniques, summarized here, are essentially the same as reported in references [1–5].

The cell, materials, and the stock solutions were the same as reported in Ref. [5]. The Gouy measurement techniques [11] were reported in detail in Refs. [1–4,12] and the Rayleigh techniques in detail in Ref. [5]. The concentration differences were small, so that the diffusion coefficients were effectively constant across the diffusion boundary. Densities were measured by pycnometry for all solutions, and used to both prepare solutions and to calculate the partial molar volumes $\overline{V}_i$ [13, 14]. The molar masses used in g·mol^{-1} were: NaCl, 58.443; $MgCl_2$, 95.211; H_2O, 18.015.

The Gouy and Rayleigh fringe patterns were captured on separate photographic plates, and the photographs taken alternately during the diffusion run. In 1989, the Gouy positions were measured on a Gaertner comparator and the Rayleigh positions on a Grant comparator. (Automation of the Gosting Diffusiometer for the Rayleigh mode [14] was not done until after the diffusiometer went to Texas Christian University in 1991.)

After Experiment 3 was completed, it was found that its Rayleigh plate was damaged and could not be read. Consequently, the 3 Gouy experiments corresponding to the 3 successful Rayleigh experiments as well as all 4 successful Gouy experiments were analyzed separately to obtain the $(D_{ij})_V$. These cases are denoted by G_4 for the 4-experiment Gouy set, by G_3 for the 3-experiment Gouy set, and by R_3 for the 3-experiment set of Rayleigh set.

The Gouy data analysis used the Albright-Miller programs [15] to obtain Q_0 and the reduced height-area ratio D_A for each run. The Gouy $(D_{ij})_V$ were obtained from these D_A and Q_0 data using the Revzin program [3]. The Rayleigh $(D_{ij})_V$ were obtained directly from the fringe position data using the Miller-Eppstein-Albright programs [5, 9, 16]. No convergence problems [5] were observed for this system.

3 Results

Table 1 contains the direct results from each individual experiment for both types of interferometry. These are the mean concentrations of each solute at the boundary $\overline{C}_1$ and $\overline{C}_2$; the concentration differences across the boundary ΔC_1 and ΔC_2; the total number of Rayleigh fringes $J_{R(exp)}$ and $J_{R(calc)}$; the refractive index fractions of NaCl α_1; and the calculated value of the time required to get from an infinitely sharp boundary to the width of the actual initial boundary at the start of the diffusion experiment Δt. Also included are data for the Gouy runs, obtained using the Albright-Miller program F3 [15]. These quantities are $J_{G(exp)}$ and $J_{G(calc)}$, and Δt. The $J_{G(exp)}$ value for experiment SW3A was obtained using the AM program F4J. The calculated values of D_A, Q_0, and Q_1 were obtained from the final values of the $(D_{ij})_V$ for the 4-experiment Gouy data set of Table 2. Finally, the measured densities of the top and bottom solutions are presented. The average concentrations in mol·dm^{-3} among all the sets were within 0.000002 for $\overline{\overline{C}}$ and 0.000001 for $\overline{\overline{C}}_1$ and $\overline{\overline{C}}_2$, as shown in Table 2.

The diagnostics from the complete Gouy data analysis suggested that the Gouy plate for experiment SW2 should be reread. The data from the reread plate, SW2ON, decreased the overall standard errors of the $(D_{ij})_V$ but did not significantly change the $(D_{ij})_V$ values.

For each data set, the values of J_{calc} are obtained from its ΔC_1, ΔC_2, and the R_i from Table 2 using the equation

$$J = R_1 \Delta C_1 + R_2 \Delta C_2 \qquad (2)$$

The R_i from Table 2 are obtained from this equation by least-squares analysis of the J_{exp}, ΔC_1, and ΔC_2 values for all experiments of that set (and are in J units). The α_1 are calculated from

$$\alpha_1 = \frac{R_1 \Delta C_1}{R_1 \Delta C_1 + R_2 \Delta C_2} \qquad (3)$$

Table 2 contains the derived Gouy and Rayleigh results for the three combined sets of data. These are the four Gouy experiments; the three successful Rayleigh experiments; and the three Gouy experiments corresponding to the three Rayleigh ones. For each set, these results consist of the overall average concentrations $\overline{\overline{C}}_i$ for all constituents including the solvent; the molalities m_i at the total concentration $\overline{\overline{C}}$; the least-squares parameters $\overline{d}$, H_1, and H_2 of the fit of all the densities of that set (from Table 1) to the equation

$$d = \overline{d} + H_1 \left(C_1 - \overline{\overline{C}}_1\right) + H_2 \left(C_2 - \overline{\overline{C}}_2\right) \qquad (4)$$

and the $\overline{V}_i$ calculated from the equations in Ref. [12, 13]. The $\overline{V}_i$ are used to convert the solvent-fixed $(D_{ij})_0$ to the volume-fixed $(D_{ij})_V$ using equations in Ref. [13]. The λ_i are the eigenvalues of the $(D_{ij})_V$ matrix and correspond to the quantity $1/s_i^2$ of previous papers in this series. The quantity S_A is a diagnostic whose absolute value must be greater than about 25 $m^{-1} \cdot s^{1/2}$ for easy convergence of the non-linear least-squares procedures for both interferometric methods. Finally, Table 2 contains the volume-fixed $(D_{ij})_V$ and their standard errors from the least-squares analyses as well as the calculated solvent-fixed $(D_{ij})_0$. These analyses were done in 1989–1992 and 1997. A rule of thumb given previously [2–5, 17, 18] is that the actual accuracy ("realistic" error) of each $(D_{ij})_V$ is about 4 times its statistical standard error (SE) from the least-squares analysis.

Table 3 shows the $(D_{ij})_V$ values for the two Gouy sets G_4 (4 experiments) and G_3 (3 experiments) and the Raleigh R_3 (3 experiments) reported here, as well as the results from the two earlier measurements [8, 9] at essentially the same concentrations.

The published standard errors of our second investigation [9] were calculated incorrectly. Fortunately, the computer card images of the fringe positions, *etc*., were still available, and the data analysis was redone correctly in 1997. This 5-experiments case is denoted by T_5. The $(D_{ij})_V$ values were unchanged within the round-off errors, and the standard errors of $(0.0020, 0.0033, 0.0007, 0.0010) \times 10^9$ $m^2 \cdot cm^{-1}$ for D_{11}, D_{12}, D_{21}, and D_{22}, respectively, are now correct. The same rule of thumb for "realistic" errors of $4 \times$ SE was applied here.

Unfortunately, the cards or card images from our first investigation [8] were no longer available. This 4-experiments case is denoted by E_4. For lack of the statistical errors, the error estimates were assumed to be the same as for the corrected second investigation (T_5) above.

4 Discussion

As expected from the same cell, same solutions, and the high precision optical systems, the Gouy and Rayleigh *J* values differ by not more than 0.04 fringe, as shown in Table 1.

Table 2 shows that the corresponding $(D_{ij})_V$ from the two sets of Gouy experiments G_4 and G_3 are quite close, and their differences are within their combined errors using the "realistic" errors of $4 \times$ SE of each $(D_{ij})_V$ (details not shown). The same is true between the corresponding $(D_{ij})_V$ of the Rayleigh R_3 and Gouy G_4 sets. However, the differences between R_3 and G_3 for $(D_{12})_V$ and $(D_{22})_V$ are not within their combined errors by about a factor of two, but percentage wise are only about 5% and 1% different, respectively. Overall the agreement among the new results is quite satisfactory.

We note that the values of $(D_{11})_V$ and $(D_{21})_V$ for G_3, G_4, and R_3 agree well within their only 1 SE values**.** Similar good agreement for the values of $(D_{11})_V$ and $(D_{21})_V$, and less good agreement for $(D_{12})_V$ and $(D_{22})_V$, were also observed for our previous measurements for NaCl-$MgCl_2$-H_2O [5].

Table 3 compares the $(D_{ij})_V$ values from our Gosting Diffusiometer, sets G_4, G_3, and R_3, and those from our first (previously unpublished) results E_4 [8] and the second (published) results T_5 at essentially the same concentrations [9]. Surprisingly, the older E_4 $(D_{ij})_V$ are closer to our newer results than are the later T_5 $(D_{ij})_V$. The SE values for each T_5 $(D_{ij})_V$ were given above, and, as noted above, we take the "realistic" errors for both E_4 and T_5 as $4 \times$ SE of the corresponding T_5 $(D_{ij})_V$. We find that the differences in the corresponding $(D_{ij})_V$ for E_4 with those for G_4 and G_3 are within their combined "realistic" errors, and are within or close to those for R_3. The agreements for T_5 with G_4, G_3, and R_3 are not within the combined "realistic" errors for any of the new results, although the $(D_{ij})_V$ values are similar. It is possible that we have underestimated the systematic errors for T_5 arising from the double-pass optics problem in the earlier experiments, from the errors from the analysis for Mg, or from making up solutions.

Table 4 shows the mean values of various combinations of diffusion coefficients obtained with the Gosting Diffusiometer $(D_{ij})_V$. They are all close, the largest variation being for $(D_{12})_V$. We recommend the mean of the G_4 and R_3 values for the diffusion coefficients of the seawater composition of NaCl-$MgCl_2$-H_2O; namely, $(D_{11})_V = 1.432 \times 10^{-9}$ $m^2 \cdot sec^{-1}$, $(D_{12})_V = 0.750 \times 10^{-9}$ $m^2 \cdot sec^{-1}$, $(D_{21})_V = 0.0185 \times 10^{-9}$ $m^2 \cdot sec^{-1}$, and $(D_{22})_V = 0.728 \times 10^{-9}$ $m^2 \cdot sec^{-1}$.

This system, like other NaCl-$MgCl_2$-H_2O compositions that are dilute in $MgCl_2$, has a very large D_{12} cross-term, here about 3% larger than D_{22}. This can considerably influence diffusive transport in unexpected ways in some situations, as is discussed elsewhere [9]. Consequently, the common simplifying assumption that cross-terms are zero can be seriously in error.

We note that the Onsager Reciprocal Relations are satisfied for all of the Gosting diffusiometer results within the experimental error based on the error of $4 \times$ SE for each $(D_{ij})_V$ and assuming that the error of each activity coefficient derivative is 5% of the derivative's value. However, the details of these calculations and the similar satisfaction of the Onsager Reciprocal Relations for the other 25 NaCl-$MgCl_2$-H_2O compositions [1–5] will be reported elsewhere. We also note that Leaist [19] has extended the diffusion coefficient measurements to very low concentrations using the conductimetric method, and Rard and Miller [20] reported an extensive isopiestic study needed for calculation of the chemical potential derivatives (the driving force for diffusion) required for this analysis.

We also note that we have carried out an extensive series of diffusion coefficient measurements for another ternary seawater subsystem, NaCl-Na_2SO_4-H_2O at 25.00 °C. A total of 28 compositions were investigated. See the final paper of this series, Ref. [21], for references to the earlier papers. Values of the cross-term diffusion coefficient D_{12} is larger than D_{22} at certain solute ratios and total concentrations, as observed for the NaCl-$MgCl_2$-H_2O system, indicating that this may be a common occurrence for aqueous mixed electrolytes of different charge type.

Acknowledgements

We thank Prof. John Albright for helpful discussions. We also thank Dr. Lee B. Eppstein for his early work in perfecting our use of Rayleigh interferometry for ternary systems. This work was performed under the auspices of the U. S Department of Energy, UC, LLNL under Contract W-7403-Eng-48.

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Table 1 Data from Rayleigh and Gouy diffusion measurements on NaCl (0.48877 mol·dm^{-3})-$MgCl_2$ (0.05110 mol·dm^{-3})-H_2O at 25 °C (seawater composition)[a]

Experiment	SW1A	SW2ON	SW3A	SW4A
$\overline{C}_1$	0.48881_2	0.48873_8	0.48877_2	0.48875_8
$\overline{C}_2$	0.05110_0	0.05108_8	0.05110_0	0.05109_8
ΔC_1	0.000153	0.179311	0.143834	0.035933
ΔC_1	0.074996	0.000005	0.015029	0.060137
J_R(exp)	79.963	79.951	-	80.243
J_R(calc)	80.038	79.970	-	80.149
α_1	0.00085	0.99920	-	0.19993
Δt	16.30	11.21	-	19.44
J_G(exp)	80.002	79.915	79.959[b]	80.200
J_G(calc)	80.040	79.843	80.068	80.125
α_1	0.00085	0.99992	0.79983	0.19967
Δt	14.51	9.50	14.49	13.86
$10^9 \times D_A$(exp)	0.9482	1.4924	1.3581	1.0304
$10^9 \times D_A$(calc)	0.9486	1.4962	1.3539	1.0305
$10^4 \times Q_0$(exp)	81.67	–13.89	29.24	83.31
$10^4 \times Q_0$(calc)	81.27	–14.31	29.61	83.74
$10^4 \times Q_1$(exp)	39.22	–5.98	12.96	39.22
$10^4 \times Q_1$(calc)	38.23	–6.04	12.79	38.59
d(top)	1.017871	1.017182	1.017317	1.017726
d(bottom)	1.023603	1.024341	1.024189	1.023738
A-M code	F3	F3	F3	F3

[a] Gouy experimental values are from D_A(extrap), Q_0(average), and Q_1(average), and the Gouy value of Δt is from the plot of "apparent" D_A *versus* 1/(experimental time). Calculated Gouy values of α_1, D_A, Q_0, and Q_1 are derived from all four experiments. Calculated Rayleigh values of α_1 are from the three experiments. Units are: C, mol·dm^{-3}; t, s; D_A, m^2·sec^{-1}; d, g·cm^{-3}.
[b] J obtained from the Albright-Miller program F4J [15].

Table 2 Experimental results[a] for
NaC1 (0.48877 mol·dm^{-3})-MgC1$_2$ (0.05110 mol·dm^{-3})-H$_2$O at 25 °C (seawater composition)

	Gouy (4 Experiments) G_4	Gouy (3 Experiments) G_3	Rayleigh (3 Experiments) R_3
$\overline{\overline{C}}$	0.539866	0.539864	0.539864
$\overline{\overline{C}}_1$	0.488770	0.488769	0.488769
$\overline{\overline{C}}_2$	0.051096	0.051095	0.051095
$\overline{\overline{C}}_0$	54.8046	54.8045	54.8045
$m_1(\overline{\overline{C}}_1, \overline{\overline{C}}_2)$	0.495049	0.495049	0.495049
$m_2(\overline{\overline{C}}_1, \overline{\overline{C}}_2)$	0.051753	0.051752	0.051752
H_1	39.874	39.914	39.914
H_2	76.255	76.261	76.261
$\overline{d}$	1.020746	1.020744	1.020744
$\overline{V}_1$	18.618	18.579	18.579
$\overline{V}_2$	19.006	19.001	19.001
$\overline{V}_0$	18.063	18.063	18.063
R_1	445.240	445.703	445.948
R_2	1066.357	1066.425	1066.300
$10^9 \times \lambda_1$	1.4527	1.4500	1.4495
$10^9 \times \lambda_2$	0.7048	0.7037	0.7128
S_A	–66.22	–65.92	–66.21
$10^9 \times (D_{11})_v$	1.4329±0.0037	1.4305±0.0027	1.4309±0.0013
$10^9 \times (D_{12})_v$	0.7665±0.0059	0.7688±0.0033	0.7343±0.0027
$10^9 \times (D_{21})_v$	0.0188±0.0007	0.0184±0.0008	0.0182±0.0004
$10^9 \times (D_{22})_v$	0.7246±0.0024	0.7231±0.0010	0.7315±0.0007
$10^9 \times (D_{11})_0$	1.4462	1.4438	1.4442
$10^9 \times (D_{12})_0$	0.7804	0.7826	0.7479
$10^9 \times (D_{21})_0$	0.0202	0.0198	0.0196
$10^9 \times (D_{22})_0$	0.7260	0.7246	0.7329

[a] Units: all C_i in mol·dm^{-3}; all m_i in mol·(kg H$_2$O)$^{-1}$; H_i in g·mo1^{-1}; d in g·cm^{-3}; $\overline{V}_i$ in cm^3·mol^{-1}; R_i in dm^3·mo1^{-1}; S_A in m^{-1}·s$^{1/2}$; λ_i, $(D_{ij})_v$, $(D_{ij})_0$ in m^2·sec^{-1}. Divide the values of H_i of this table by 10^3 to get d in g·cm^{-3} from Eq. (4) when the C_i are in mol·dm^{-3}.

Table 3 Comparison of diffusion coefficient data for
NaCl (0.4888 mol·dm^{-3})-$MgCl_2$ (0.0511 mol·dm^{-3})-H_2O at 25 °C (seawater composition)

	Gouy[a] 4 Expts G_4	Gouy[a] 3 Expts G_3	Rayleigh[a] 3 Expts R_3	Eppstein[b] 4 Expts E_5	Ting[b] 5 Expts T_5
$\overline{\overline{C_1}}$	0.488770	0.488769	0.488769	0.48878	0.48876
$\overline{\overline{C_2}}$	0.051096	0.051095	0.051095	0.05114	0.05109
$10^9 \times (D_{11})_V$	1.4329	1.4305	1.4309	1.4427	1.4086
$10^9 \times (D_{12})_V$	0.7665	0.7688	0.7343	0.7557	0.6991
$10^9 \times (D_{21})_V$	0.0188	0.0184	0.0182	0.0151	0.0250
$10^9 \times (D_{22})_V$	0.7246	0.7231	0.7315	0.7297	0.7411

[a] Units of $(D_{ij})_V$, m^2·sec^{-1}; units of $\overline{\overline{C_i}}$, mol·dm^{-3}. The $(D_{ij})_v$ for the Gosting diffusiometer experiments are taken from Table 2. The Ting *et al*. $(D_{ij})_v$ are taken from Ref. [9]. The Eppstein and Miller $(D_{ij})_v$ are from [8] (unpublished).
[b] Measurements from Gosting Diffusiometer.
[c] Measurements from Beckman-Spinco Model H in Rayleigh mode.

Table 4 Some mean and recommended $(D_{ij})_V$ values from the Gosting diffusiometer for
NaCl (0.48877 mol·dm^{-3})-$MgCl_2$ (0.05110 mol·dm^{-3})-H_2O (seawater composition)

Means	$10^9 \times (D_{11})_V$	$10^9 \times (D_{12})_V$	$10^9 \times (D_{21})_V$	$10^9 \times (D_{22})_V$
all 3 sets G_4, G_3, R_3	1.4314	0.7565	0.0185	0.7264
both 3 expt sets G_3, R_3	1.4307	0.7516	0.0183	0.7273
both Gouy sets G_4, G_3	1.4317	0.7676	0.0186	0.7238
4-Gouy and 3-Rayleigh expts G_4, R_3	1.4319	0.7504	0.0185	0.7280
Recommended[a]	1.432	0.750	0.0185	0.728

[a] This recommendation is the mean of the 4-Gouy and 3-Rayleigh results. Units of $(D_{ij})_V$, m^2·sec^{-1}.